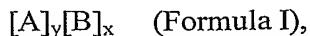
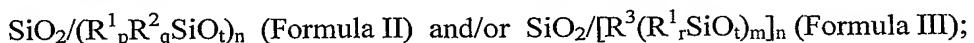


What is claimed is:

1. A material for chromatographic separations comprising a porous inorganic/organic hybrid monolith, said monolith having an interior area and an exterior surface, wherein said monolith is represented by:

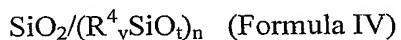


wherein x and y are whole number integers and A is



wherein R^1 and R^2 are independently a substituted or unsubstituted C_1 to C_7 alkyl group, or a substituted or unsubstituted aryl group, R^3 is a substituted or unsubstituted C_1 to C_7 alkylene, alkenylene, alkynylene, or arylene group bridging two or more silicon atoms, p and q are 0, 1, or 2, provided that $p + q = 1$ or 2, and that when $p + q = 1$, $t = 1.5$, and when $p + q = 2$, $t = 1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2; and n is a number from 0.01 to 100;

B is :



wherein R^4 is hydroxyl, fluorine, alkoxy, aryloxy, substituted siloxane, protein, peptide, carbohydrate, nucleic acid, or combinations thereof, R^4 is not R^1 , R^2 , or R^3 ; v is 1 or 2, provided that when $v = 1$, $t = 1.5$, and when $v = 2$, $t = 1$; and n is a number from 0.01 to 100;

said interior of said monolith having a composition of A; said exterior surface of said monolith having a composition represented by A and B, and wherein said exterior composition is between about 1 and about 99% of the composition of B and the remainder comprising A.

2. The material of claim 1 wherein said exterior surface has a composition that is between about 50 and about 90% of composition B, with the remainder comprising composition A.

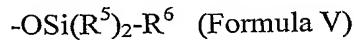
3. The material of claim 1 wherein said exterior surface has a composition that is between about 70 and about 90% of composition B, with the remainder comprising composition A.

4. The material of claim 1 wherein R^4 is hydroxyl.

5. The material of claim 1 wherein R^4 is fluorine.

6. The material of claim 1 wherein R⁴ is methoxy.

7. The material of claim 1 wherein R⁴ is



wherein R⁵ is a C₁ to C₆ straight, cyclic, or branched alkyl, aryl, or alkoxy group, a hydroxyl group, or a siloxane group, and R⁶ is a C₁ to C₃₆ straight, cyclic, or branched alkyl, aryl, or alkoxy group, wherein R⁶ is unsubstituted or substituted with one or more moieties selected from the group consisting of halogen, cyano, amino, diol, nitro, ether, carbonyl, epoxide, sulfonyl, cation exchanger, anion exchanger, carbamate, amide, urea, peptide, protein, carbohydrate, nucleic acid functionalities, and combinations thereof.

8. The material of claim 7 wherein R⁶ is a C₁₈ group.

9. The material of claim 7 wherein R⁶ is a cyanopropyl group.

10. The material of claim 1, having a specific surface area of about 50 to about 800 m²/g.

15 11. The material of claim 1, having a specific surface area of about 190 to about 520 m²/g.

12. The material of claim 1, having specific pore volumes of about 0.5 to about 2.5 cm³/g.

20 13. The material of claim 1, having specific pore volumes of about 1 to about 2 cm³/g.

14. The material of claim 1, having an average pore diameter of about 35 to 500 Å.

15. The material of claim 1, having an average pore diameter of about 100 to 300 Å.

25 16. The material of claim 1, having been surface modified by polymer coating.

17. A method of performing a chromatographic separation comprising contacting a sample with the material of claim 1.

30 18. The method of claim 17, wherein the sample is passed through a chromatographic column containing the material of claim 1.

19. The material of claim 7, having a surface concentration of R⁶ greater than about 1.0 μmol/m².

20. The material of claim 7, having a surface concentration of R⁶ greater than about 2.0 $\mu\text{mol}/\text{m}^2$.

21. The material of claim 7, having a surface concentration of R⁶ greater than about 3.0 $\mu\text{mol}/\text{m}^2$.

5 22. The material of claim 7, having a surface concentration of R⁶ between about 1.0 and 3.4 $\mu\text{mol}/\text{m}^2$.

23. The material of claim 20, having a specific surface area of about 50 to about 800 m^2/g .

10 24. The material of claim 20, having a specific surface area of about 190 to about 520 m^2/g .

25. The material of claim 20, having specific pore volumes of about 0.5 to about 2.5 cm^3/g .

26. The material of claim 20, having specific pore volumes of about 1 to about 2 cm^3/g .

15 27. The material of claim 20, having an average pore diameter of about 35 to 500 \AA .

28. The material of claim 20, having an average pore diameter of about 100 to 300 \AA .

20 29. The material of claim 20, which have been surface modified by polymer coating.

30. A method of performing a separation comprising contacting a sample with the material of claim 20.

31. The method of claim 29, wherein the sample is passed through a chromatographic column containing the material of claim 20.

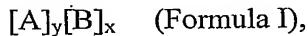
25 32. A separation device comprising the material of claim 1.

33. The separation device of claim 30, said device is selected from the group consisting of chromatographic columns, thin layer chromatographic plates, filtration membranes, sample clean up devices, solid phase organic synthesis supports, and microtiter plates.

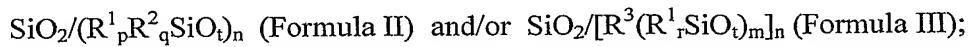
30 34. The material of claim 1, wherein the monolith has a chromatographically enhancing pore geometry.

35. The separation device of claim 30, wherein the monolith has a chromatographically enhancing pore geometry.

36. A method of preparing material for chromatographic separations comprising a porous inorganic/organic hybrid monolith, said monolith having an interior area and an exterior surface, wherein said monolith is represented by:



5 wherein x and y are whole number integers and A is



10 wherein R^1 and R^2 are independently a substituted or unsubstituted C_1 to C_7 alkyl group, or a substituted or unsubstituted aryl group, R^3 is a substituted or unsubstituted C_1 to C_7 alkylene, alkenylene, alkynylene, or arylene group bridging two or more silicon atoms, p and q are 0, 1, or 2, provided that $p + q = 1$ or 2, and that when $p + q = 1$, $t = 1.5$, and when $p + q = 2$, $t = 1$; r is 0 or 1, provided that when $r = 0$, $t = 1.5$, and when $r = 1$, $t = 1$; m is an integer greater than or equal to 2; and n is a number from 0.01 to 100;

B is :



wherein R^4 is hydroxyl, fluorine, alkoxy, aryloxy, substituted siloxane, protein, peptide, carbohydrate, nucleic acid, or combinations thereof, R^4 is not R^1 , R^2 , or R^3 ; v is 1 or 2, provided that when $v = 1$, $t = 1.5$, and when $v = 2$, $t = 1$; and n is a number from 0.01 to 100;

20 said interior of said monolith having a composition of A; said exterior surface of said monolith having a composition represented by A and B, and wherein said exterior composition is between about 1 and about 99% of the composition of B and the remainder comprising A;

the method comprising:

25 a) preparing an aqueous solution of a mixture of one or more organoalkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst, and a surfactant or combination of surfactants to produce a polyorganoalkoxysiloxane;

b) incubating said solution, resulting in a three-dimensional gel having a continuous, interconnected pore structure;

c) aging the gel at a controlled pH and temperature to yield a solid monolith material;

d) rinsing the monolith material with an aqueous basic solution at an elevated temperature;

- e) rinsing the monolith material with water followed by a solvent exchange;
- f) drying the monolith material at room temperature drying and at an elevated temperature under vacuum; and
- g) replacing one or more surface C₁ to C₇ alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted C₁ to C₇ alkylene, alkenylene, alkynylene, or arylene groups of the monolith with hydroxyl, fluorine, alkoxy, aryloxy, or substituted siloxane groups.

5 37. The method of claim 34, further comprising modifying the pore structure of the monolith material by hydrothermal treatment, following step d).

10 38. The method of claim 34, wherein said replacing involves reacting the hybrid monolith with aqueous H₂O₂, KF, and KHCO₃ in an organic solution.

39. The method of claim 34, wherein the molar ratio of said organotrialkoxysilane and tetraalkoxysilane is about 100:1 to 0.01:1.

15 40. The method of claim 34, wherein said surfactant is an alkylphenoxypropoxyethoxyethanol and or a Pluronic block copolymer.

41. The method of claim 34, wherein said solution in step a) further comprises a porogen.

42. The method of claim 34, wherein said tetraalkoxysilane is tetramethoxysilane or tetraethoxysilane.

20 43. The method of claim 34, wherein said replacing comprises modifying the surface of the hybrid monolith with a surface modifier.

25 44. The method of claim 41, wherein the surface modifier is Z_a(R')_bSi-R:
where Z = Cl, Br, I, C₁ - C₅ alkoxy, dialkylamino; a and b are each an integer from 0 to 3 provided that a + b = 3; R' is a C₁ - C₆ straight, cyclic or branched alkyl group; and R is a functionalizing group

45. The method of claim 42 wherein R' is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, t-butyl, sec-butyl, pentyl, isopentyl, hexyl and cyclohexyl.

30 46. The method of claim 42 wherein the functionalizing group R is selected from group consisting of alkyl, aryl, cyano, amino, diol, nitro, cation or anion exchange groups, and embedded polar functionalities.

47. The method of claim 42, wherein the surface modifier is a haloorganosilane.

48. The method of claim 45, wherein the haloorganosilane is octyldimethylchlorosilane or octadecyldimethylchlorosilane.

49. The method of claim 34, further comprising end-capping the surface of the hybrid monolith.

50. The method of claim 47, the surface of the hybrid monolith is endcapped with a trialkylhalosilane.

51. The method of claim 48, wherein the trialkylhalosilane is trimethylcholosilane.

52. A material for chromatographic separations comprising a porous 10 inorganic/organic hybrid monolith, said monolith having an interior area and an exterior surface, wherein said monolith is represented by:

$$[A]_y[B]_x \quad (\text{Formula I}),$$

wherein x and y are whole number integers and A is

$$\text{SiO}_2/(R^1_p R^2_q \text{SiO}_t)_n \quad (\text{Formula II}) \text{ and/or } \text{SiO}_2/[R^3(R^1_r \text{SiO}_t)_m]_n \quad (\text{Formula III});$$

15 wherein R¹ and R² are independently a substituted or unsubstituted C₁ to C₇ alkyl group, or a substituted or unsubstituted aryl group, R³ is a substituted or unsubstituted C₁ to C₇ alkylene, alkenylene, alkynylene, or arylene group bridging two or more silicon atoms, p and q are 0, 1, or 2, provided that p + q = 1 or 2, and that when p + q = 1, t = 1.5, and when p + q = 2, t = 1; r is 0 or 1, provided that when r = 0, t = 1.5, 20 and when r = 1, t = 1; m is an integer greater than or equal to 2; and n is a number from 0.01 to 100;

B is :

$$\text{SiO}_2/(R^4_v \text{SiO}_t)_n \quad (\text{Formula IV})$$

25 wherein R⁴ is hydroxyl, fluorine, alkoxy, aryloxy, substituted siloxane, protein, peptide, carbohydrate, nucleic acid, or combinations thereof, R⁴ is not R¹, R², or R³; v is 1 or 2, provided that when v = 1, t = 1.5, and when v = 2, t = 1; and n is a number from 0.01 to 100;

30 said interior of said monolith having a composition of A; said exterior surface of said monolith having a composition represented by A and B, and wherein said exterior composition is between about 1 and about 99% of the composition of B and the remainder comprising A;

said material prepared by a process comprising:

- a) preparing an aqueous solution of a mixture of one or more organoalkoxysilanes and a tetraalkoxysilane in the presence of an acid catalyst, and a surfactant or combination of surfactants to produce a polyorganoalkoxysiloxane;
- 5 b) incubating said solution, resulting in a three-dimensional gel having a continuous, interconnected pore structure;
- c) aging the gel at a controlled pH and temperature to yield a solid monolith material;
- 10 d) rinsing the monolith material with an aqueous basic solution at an elevated temperature;
- e) rinsing the monolith material with water followed by a solvent exchange;
- f) drying the monolith material at room temperature drying and at an elevated temperature under vacuum; and
- 15 g) replacing one or more surface C₁ to C₇ alkyl groups, substituted or unsubstituted aryl groups, substituted or unsubstituted C₁ to C₇ alkylene, alkenylene, alkynylene, or arylene groups of the monolith with hydroxyl, fluorine, alkoxy, aryloxy, or substituted siloxane groups.

53. A method of forming a porous inorganic/organic hybrid monolith comprising:

- 20 (a) forming a porous inorganic/organic hybrid monolith having surface silicon-alkyl groups;
- (b) replacing one or more surface silicon-alkyl groups of the hybrid monolith with hydroxyl groups;
- (c) replacing one or more surface silicon-alkyl groups with halo groups;
- 25 (d) bonding one or more substituted siloxane groups to the surface of the hybrid monolith; and
- (e) end-capping the surface of the hybrid monolith with trialkylhalosilane.

54. The method of claim 51, wherein alkyl is methyl and halo is chloro.

55. The method of claim 51, wherein bonding one or more substituted siloxane groups to the surface of the hybrid monolith produces a bonded phase.

30 56. The method of claim 53, wherein the bonded phase comprises octadecyldimethylsiloxane groups (ODS) or CN.